Natural Rubber / Epoxidised Natural Rubber / Polyvinyl Chloride Ternary Blends

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ABSTRACT

Blends of polyvinyl chloride(PVC) with natural rubber (NR) at all compositions were found to be incompatible and show poor mechanical properties. Nevertheless, PVC with epoxidised natural rubber(ENR) formed miscible blends with good mechanical properties. In recent report, PVC-ENR blends were shown to form cross linked during moulding at elevated temperatures in the absence of any cross linking agent, which

ascribe to promising properties. Therefore, to achieve enhance mechanical performance of the blends, phases must be compatible to certain extent.

A study was conducted to improve the poor properties of the immiscible NR/PVC system by the insertion of ENR as the ternary component. Preparation of the blends was accomplished on a Brabender Plasticorder PL-2000 utilising a cam-blade mixer with silicone oil heating system. From the mechanical properties analysis, ENR insertion up to 20% showed improvement in the overall mechanical behaviour of the NR/PVC blends at 2:3, 1:1, 3:2 ratio understudied. NR/PVC dissolved readily in tetrahydrofuran(THF), whereas blends of NR/PVC containing ENR up to 20% swells which probably demonstrate the entanglement formation physically or chemically. Different type of ENR influence the blend properties whereby ENR50 is a better compatibilizer or properties modifier for NR/PVC blends.

Mixing characteristic also influence properties of the blends. Tensile performance shows that blends is the best under optimised conditions. Hardness properties however increases with the increase in speed and temperature for both ENR25 and ENR50.

Density of the blends was found to be unchanged, albeit the changes in composition and mixing condition (is 1.05 ± 0.01 g/cm^3).

INTRODUCTION

The study of ternary blends becomes increasingly important[1] with the incentive to discover new polymeric materials and/or develop practical and economic methods for recycling commodity plastic[2].

Miscibility of the constituent polymers is often a necessity for forming successful blends. One of the commercially important and miscible polymer blend is that of nitrile butyl rubber (NBR) and polyvinyl chloride (PVC). NBR/PVC blends can be conveniently milled, extruded and compression molded using traditional processing equipments for natural and synthetic rubbers[3]. PVC in the blends improves ozone, thermal aging and chemical resistance of NBR in applications like feed hose covers, gaskets, conveyor belt covers, printing roll covers etc. Also , PVC vastly improves tear resistance, tensile properties and abrasion resistance. It also imparts flame-retardant character, improves finishing surface and adds glossing on the extruded stock. Whereas, NBR acts as a permanent plasticizer for PVC in applications like wire and cable insulation, bond liners for oil containment, food containers, and etc.

Besides NBR, epoxidised natural rubber (ENR) has been demonstrated by previous researcher to form miscible blends with polyvinyl chloride[4] and chlorinated polyolefins[5]. For the same reason, ENR was shown[6] to be miscible with polymeric resins (novolac) containing acidic hydroxyls. Similar results were obtained with epoxidised polybutadiene[7].

Realising the role played by epoxidised polymer in forming a compatibilised blends a study was made to explore the possibility of ENR serving as a compatibilizer for the incompatible binary NR/PVC pairs to obtain a ternary system. Besides the possibility of acting as a compatibilizer, ENR might strongly act as a polymeric properties modifier to the binary blend system.

The present study was carried out on a Brabender Plasticorder. A Brabender Plasticorder has been used extensively for assessing the fusion characteristics, mechanical and thermal stability, and characteristic of the polymers. Initially, the processing or mixing characteristics of the blends were studied, such as the speed, temperature and composition. The results are correlated with the mechanical properties and swelling behaviour of the blends as compared to the binary system.

EXPERIMENTAL METHOD

Materials

The materials used are shown in Table 1.

Table 1 : Materials used.

Materials	Specifications
SMR5	Standard Malaysian Rubber of Grades 5 obtained from Lee Rubber, Skudai, Johore.
PVC	Powder, suspension polymerised, K value -66 from Industrial Resin Malaysia, Johore.
ENR25	Epoxidised Natural Rubber of 25% epoxidation level, obtained from RRIM.
ENR50	Epoxidised Natural Rubber of 50% epoxidation level, obtained from RRIM.
Tetrahydrofuran	Grade, extra pure from Merck.

Blends preparation

Blends were prepared in a Laboratory Internal Mixer Brabender Plasticorder model PL-2000-6 using cam-blade with heated silicone oil circulation. The required weight of unstabilised PVC powder were charged into the mixing chamber. Preheating was allowed for three minutes. After three minutes regular strip of rubbery component was fed into the mixing

chamber. The mix was blended for seven minutes before dumping the blend. Density of the prepared blends were measured using a density balance.

Mechanical testing

Blends were moulded on hot press for three minutes and water cooled. Preparations and testing of specimens were performed in accordance to ASTM D412-87, with crosshead speed of 50mm/min at 24 °C on Lloyd Instrument MTM (Model L1000R). Average of five samples were tested for each measurement. Hardness test was conducted using Karl Frank Hardness Testing Instrument 38209 according to ASTM 1415.

Gel determination and swelling index

Solvent insoluble gel was measured by dissolving 0.39 to 0.41 gram of the prepared blend (cut into strips of 1mm x 5mm) in 40ml tetrahydrofuran. The blends were left to stand for 20 hr at 25 °C ±2 °C in the dark. The gel formed was filtered through borosilicate glass wool. Exactly 10ml of the filtered liquid was pipetted into a dried and weighted aluminium dish. The dish was then placed on an electric hot plate at 100 °C ±10 °C which alternately heated and weighed to the nearest 0.1 mg until a constant mass was achieved.

Gel content was calculated as follows,

$$A \times 4 = B$$

Gel % = (C-B)/C X 100

where,

A = mass of the dried sol, 10 cm^3 volume.

B = mass of the total dried sol and.

C = mass of the original sample.

The filtered swollen gel was removed from traces of solvent and quickly transferred into a well-cap weighing bottle and weighed. This represents the swollen gel. Determination of the swelling index was performed as follows,

Swelling index = E/D

where,

E = mass of the swollen gel,

D = (C-B) ,

C = mass of original sample,

B = mass of the dried sol (4XA),

D = mass of dried gel.

Both results were obtained from the average of two determinations.

RESULTS AND DISCUSSIONS

Studies on the processing conditions were first determined before proceeding with the optimum blends preparation. Processing parameters which influence the phase morphology and final strength properties of

Brabender mixed products are temperature, speed, mixing time, and total volume of the mixed component.

In the study of the processing conditions, blends containing 2:3 ratio of SMR5/PVC with 16.7% compatibilizer or modifier was used. Rheological performance of the blends was based on the Brabender studies only as proposed by Das (1986)[8].

a) Brabender torque and stock temperature

Generally, Figures 1 b and c show a sharp decrease of torque to a minimum value and gradually increase to a maximum peak was observed after the rubbery component was loaded to the preheated PVC. The maximum peak indicates `fusion' has occurred whereby polymer particles are merged into a melt. This peak is not observe in blends without PVC component as indicated by the SMR5/ENR25 torque profile. Thereafter, the torque stabilised or dropped depending on the mixing parameters used. The prolonged shearing was observed to enhance chain scission in SMR5/ENR and reduced the melt viscosity which decreases the torque in the blends (Figure 1a). The curves also demonstrate that the PVC phase provide protection from further degradation in the rubbery phase as summarised by the effect of NR/PVC ratio on torque profiles (Figure 1d).

The attainment of final steady temperature indicates a uniform exothermic mixing of the blend component and the gradual drop of temperature and

torque after prolonged mixing indicate their time dependent shear degradative action.

b) Effect of composition

Tables 2 and 3 show the mechanical properties of NR/PVC binary blends as compared to the NR/PVC blends with ENR insertion up to 20% at various NR/PVC ratio. The results demonstrate that at all compositions and NR/PVC ratio, the presence of ENR increases the tensile strength and hardness of the blends. Binary blends at all compositions and conditions are soluble in tetrahydrofuran whereas the ternary blends swell and partially soluble in tetrahydrofuran depending on the processing conditions applied. This probably indicates the absence of stable physical or chemical entanglement in binary blends. ENR in the ternary blends induces stable entanglement to occur. The swelling test shows that different ENR have different influence on the mechanical properties. ENR50 shows higher tensile strength and hardness properties and lower percent elongation at break compared to ENR25. Swell index for ENR50 is generally lower than ENR25. This indicates that ENR50 induced stronger entanglement physically or chemically.

Figures 2 and 3 demonstrate the composition effect of ENR on tensile and hardness properties. For all NR/PVC ratio, the limit for optimum tensile strength was observed at 10% of ENR25 in the blend. The ENR25 tensile properties become independent of compositions when the ENR25 content is greater than 10%. Whereas, hardness property decreases with the

increase of ENR25 content in the blends. ENR50 optimum tensile strength and hardness for NR/PVC ratio of 1:1 and 3:2 occurs at 10% ENR50 content. However, for the NR/PVC ratio of 2:3, tensile strength increases as the content of with ENR50 increases up to 20%. Hardness value maximizes at ENR50 content of 10%. Analyses show that ENR50 is more likely to act as a compatibilizer or modifier by increasing the properties of the NR/PVC system towards thermoplasticity compared to ENR25 which give rise towards rubbery properties.

Study on the concentration of the epoxy group was conducted and results demonstrate that blends depend on the individual ENR. Therefore diluting ENR50 with NR to the same epoxy concentration of ENR25 does not give similar properties as shown in Table 4.

c) Effect of temperature

The mixing torque decreases with temperature as shown by Figure 4. The figure shows that the blending time to achieve homogeneity depends on temperature. For temperature range of 160°C - 190°C, seven minutes of blending results in the degradation of blends as shown by the gradual drop in torque after fusion. This degradation could probably due to the mechanical mastication of the rubber component. At temperature higher than 180°C, the blends form a mass crumbs. This is due to the oxidative degradation of the unstabilised PVC as the blend product darken with the increase of stock temperature.

Torques obtained from the Brabender can be converted to standard rheological properties via the following equations.

$$\sigma_a = K \tau_a \quad \text{--- eqn. 1}$$

$$\gamma_a = K' S \quad \text{---- eqn. 2}$$

$$S = 2\pi/60 \times R \quad \text{--- eqn. 3}$$

where, σ_a is the shear stress, τ_a is the apparent mixing torque measured, γ_a is the apparent shear strain rate, S is the angular rotor speed, R is the rotor speed used, and K, K' are the instrumental constant.

By definition apparent shear viscosity is given by

$$\eta_a = \sigma_a/\gamma_a = K\tau_a/K' S \quad \text{----eqn. 4}$$

The temperature dependence of the viscosity follow the Arrhenius exponential relationship which relates to apparent shear viscosity.

$$K \tau_a / K' S = Ae^{E/RT} \quad \text{--------eqn 5}$$

where E is the activation energy of viscous flow. Plot of log τ_a/S verse 1/T for torque after 2 and 7 minutes shows a relationship was observed which relates to the proposed concept (Figure 5). A critical temperature (T_{cr}) by Widmayer and Meyer[9] is a temperature above which homogenous blend is obtained. The plot shows a linear relationship after 2 minutes of mixing, which was due to a minima changes occurred. A dual relationship obtained after 7 minutes of mixing was probably due to the morphological transition from heterogenous towards a homogenous blends as suggested by Nasir and Ratnam (1989)[9]. These phenomena occur for both ENR types, where T_{cr} for SMR5/PVC blends with ENR is 150°C. Below 150°C, the blends are dominated by the rubbery phase, as the fusion of

PVC is incomplete, whereas at a temperature above 150 °C, the blends are dominated by the PVC phase as the fusion is complete as shown by the degradation of rubber.

The highest tensile strength for ENR50 and ENR25 is at 150°C and 180°C, respectively. Hardness increases as the temperature increases, which demonstrates that high intermingle has occurred in the sample as shown by the low swell index and high gel content for both ENR25 and ENR50 blends system (Tables 5 and 6). At temperatures below 150°C, the blends were found to be soluble in tetrahydrofuran with traces of gel, which indicates the incomplete fusion of PVC and the presence of easily broken loose gel.

d) Effect of speed

Maintaining all other parameters constant, the speed variation results in the time variation for the blends to reach homogeneity. High rotor speed reduces the time for the blends to become homogeneous as it is easier for the blend to degrade as illustrated by the drop in torque with blending time (Figure 6). Temperature curves at various rotor speed shows similarity, whereby attainment of steady temperature is fastest at the highest rotor speed. This is consistent with that reported by Varughese et al.(1989)[10]. The decrease in torque with time at high rotor speed, ie. above 60 rpm, for the tested composition indicates the time dependent of the blends. This

time dependent can be described by the change in structure or morphology due to the degradation of the rubbery component and also by the oxidation observed.[13]

Effect of speed on mechanical properties for ENR50 are shown in Table 7, where tensile strength is the highest at speed 40 rpm and % elongation at break is also at its maximum. For ENR25, the optimum speed is at 20 rpm (Table 8). Tensile results are found to be consistent with the swelling test results, however hardness properties increases as the speed increases.

CONCLUSION

The studies show that ENR improves the properties of the incompatible NR/PVC blends and probably acts as a modifier or a compatibilizer. Generally, blends with ENR50 shows better properties compared to blends with ENR25. Results also demonstrate the importance of proper mixing parameters since mechanical and physical properties depend on these factors. The study shows that, the unstabilised PVC at high temperature and speed undergo oxidative degradation as shown in ENR50 system. This effect is less prominent in ENR25. Optimum temperature is near the PVC melt temperature, 180°C. Future studies require the addition of stabilizer to the system.

Density of the blends were measured and was found unchanged, despite the changes in composition and mixing condition, 1.05 ± 0.01 g/cm^3.

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Table 2 Properties of NR/LNR25/PVC Blends

		% LNR25 in Blends				
	Ratio	0	5	10	16.7	20
Ten. Strgh MPa	3:2	0.51	1.20	1.32	1.30	1.31
	1:1	0.90	1.35	1.40	1.50	1.50
	2:3	1.095	1.71	1.97	1.52	1.45
% elong. at brk	3:2	1712	1151	1177	1233	1206
	1:1	607	806	826	1049	1101
	2:3	160	347	588	661	732
Hard-ness Shore A Shore D	3:2	39.4	42.5	38.0	33.0	31.8
	1:1	78.8	61.3	60.6	44.5	42.2
	2:3		72.8	62.4	65.9	60.0
	2:3	36.4				
Swell index	3:2	soluble	42.12	52.00	55.69	63.20
	1:1	soluble	46.83	35.24	49.82	78.96
	2:3	soluble	39.31	59.43	43.10	52.41

Table 3 - Properties of NR/ENR50/PVC blends

		% ENR50 in the blends				
	Ratio	0	5	10	16.7	29
Ten. strgh. MPa	3:2	0.51	0.79	2.84	1.04	0.82
	1:1	0.89	1.37	1.87	1.49	1.53
	2:3	1.09	1.59	2.77	2.62	4.05
% elong. at brk	3:2	1712	894	744	785	852
	1:1	607	549	419	371	471
	2:3	160	300	141	170	310
Haro-ness Shore A	3:2	39.4	43.0	38.8	37.4	29.6
	1:1	74.8	70.6	95.4	31.8	29.6
	2:3		95.4	100	96.6	91.2
Shore D	2:3	36.4				
Swell index	3:2	soluble	31.82	35.17	33.95	43.81
	1:1	soluble	26.72	32.98	31.49	24.91
	2:3	soluble	29.64	28.78	43.62	44.27

Table 4 . Effect of epoxy group concentration.

Properties	Tensile strength MPa	% elongation at brk
SMR5/ENR50/PVC 18: 18: 24	2.88	579.5
ENR25/PVC 36: 24	0.32	1712
SMR5/ENR50/PVC 15: 15: 30	5.12	197.1
ENR25/PVC 30:30	0.28	834

Table 5: Effect of temperature on SMR5/ENR25/PVC blends

Temp C	Ten. Strgh MPa	% elong. at break	Hardness Shore A	% gel cont.	Swell index
120	1.16	773	72.8	trace	-
140	1.63	692	62.4	trace	-
150	1.52	661	65.2	11.48	43.10
160	1.46	469	62.4	7.14	43.68
180	2.09	208	72.8	11.96	16.63

Table 6 Effect of temperature on SMR5/ENR50/PVC blends

Temp C	Ten. strgh. MPa	% elong. at brk.	Hardness Shore A	% gel cont.	Swell index
120	2.09	399	83.4	trace	-
140	2.87	274	92.6	trace	-
150	3.07	170	96.6	7.61	43.62
160	2.39	116	32	6.85	38.45
180	degraded	-	-	-	-

Table 7 : Effect of speed on properties of ENR50 blend

Speed rpm.	Ten. strgh. MPa	% elong.at brk.	Hardness Shore A	% gel cont.	Swelling index
20	1.81	150	60.2	7.61	43.62
40	3.07	170	96.6	11.36	31.14
50	2.70	142	99.2	5.24	53.37
60	2.58	97	100	4.02	49.79
80	2.61	55	100	36.95	36.93

Table 8 : Effect of speed on properties of ENR25 blend

Speed rpm.	Ten. strgh. MPa	% elongat brk	Hardness Shore A	% gel cont.	Swelling index
20	1.52	661	65.2	11.48	38.86
25	1.18	662	64.6	4.92	81.86
30	1.35	674	70.1	9.71	39.49
40	1.03	592	71.2	5.25	57.88

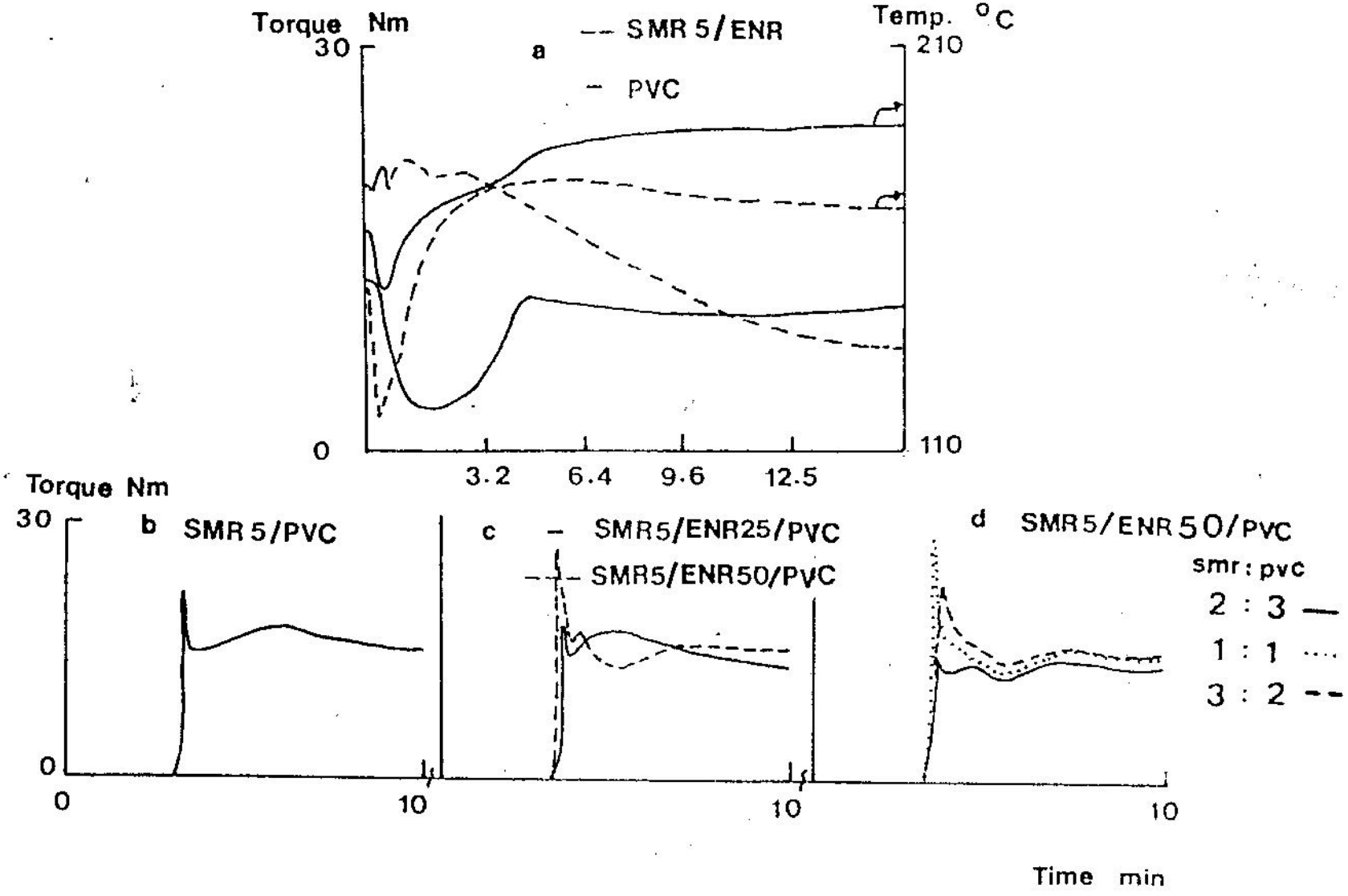

Figure 1: Torque profile of blends verses time

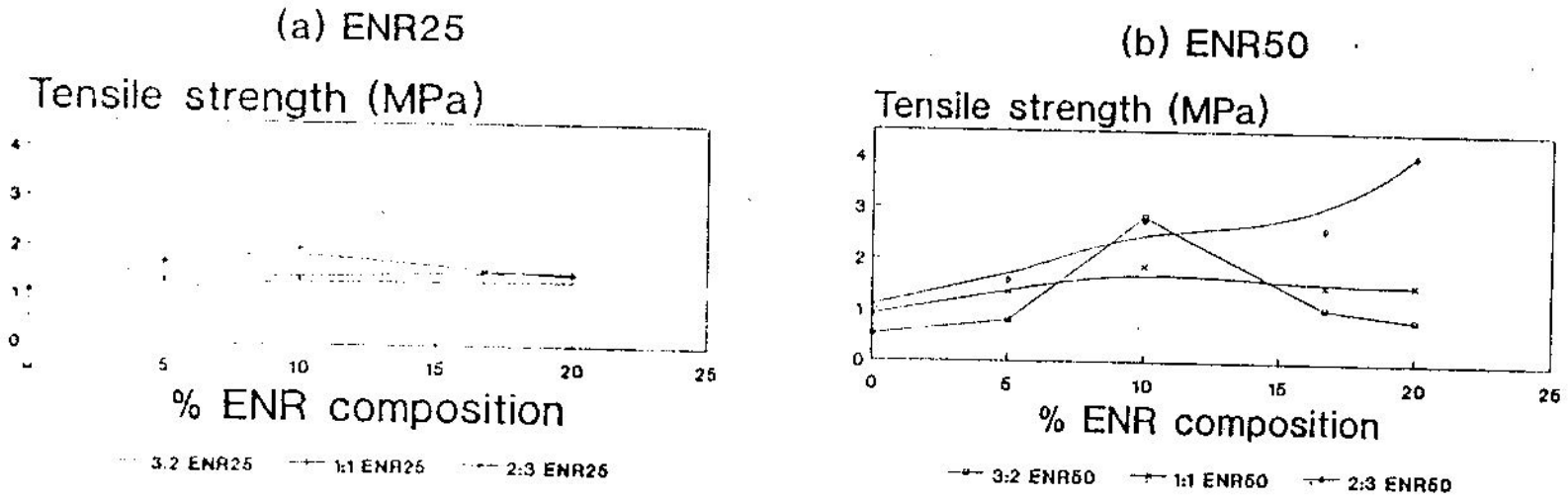

Figure 2: Tensile strength against % composition of ENR in SMR5/PVC blends.

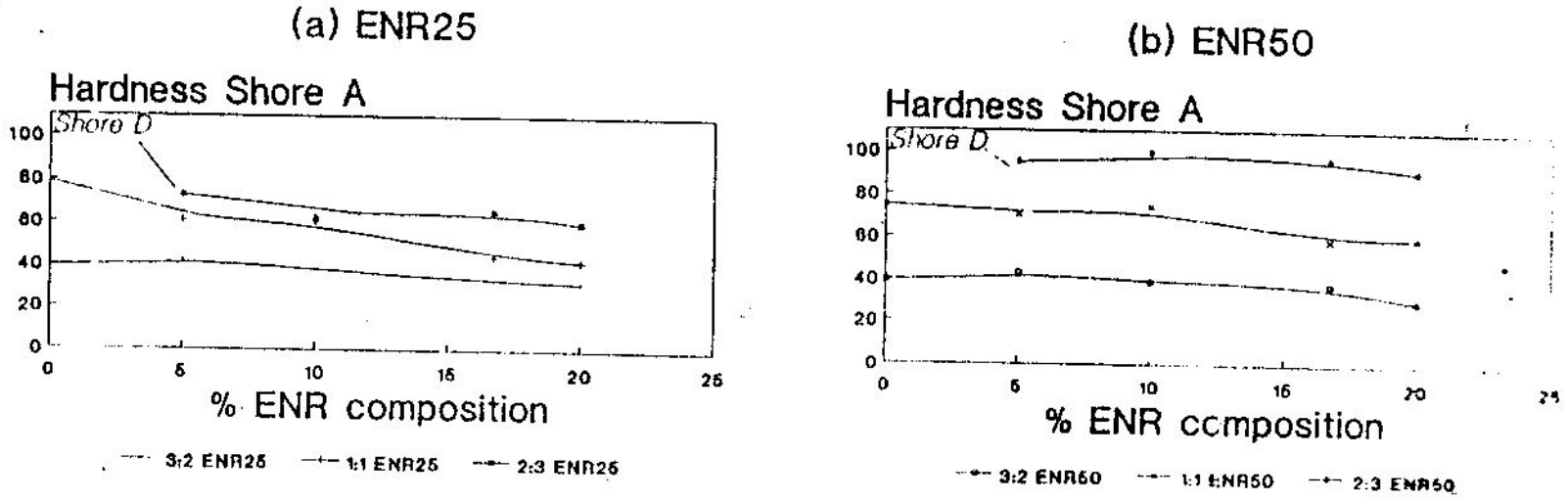

Figure 3: Shore A against % composition of ENR in SMR5/PVC blends.

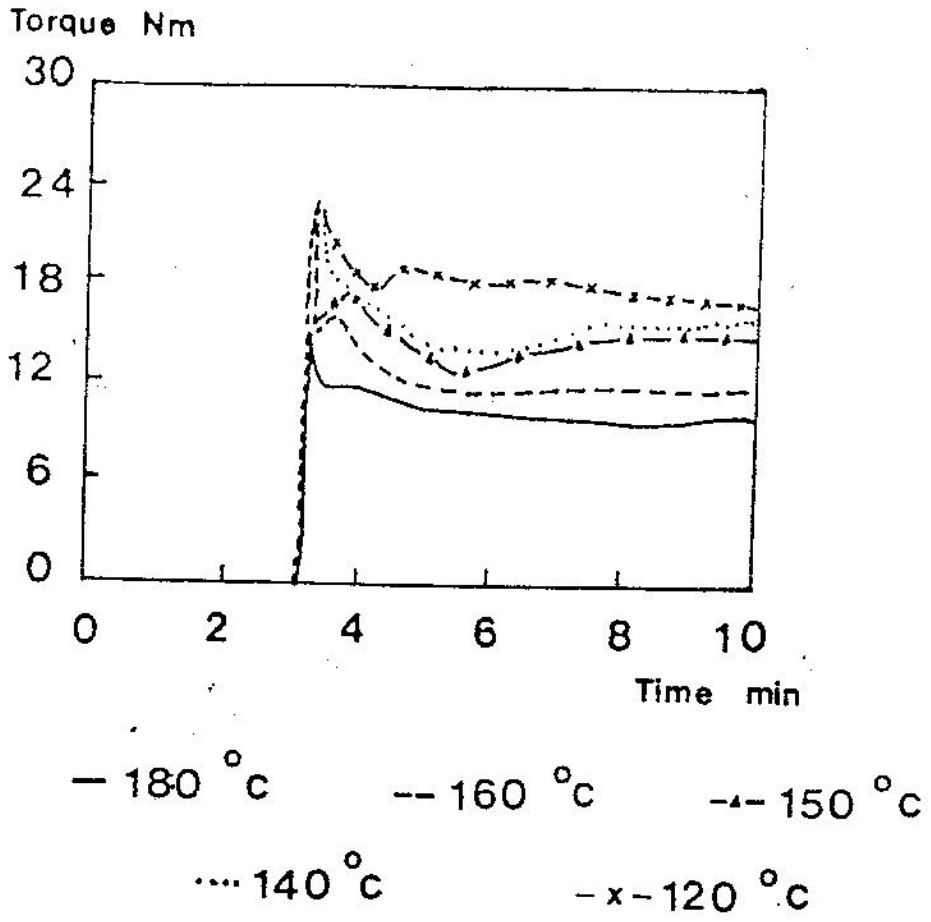

Figure 4: PVC/ENR50/SMR5 (30:10:20) torque profile at various temperature against time.

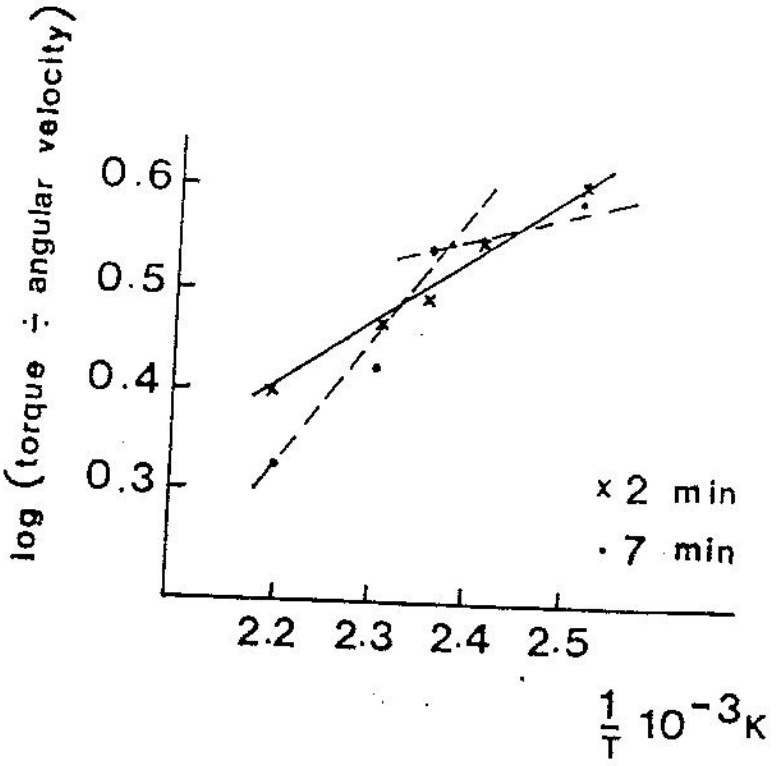

Figure 5: Graph of log τ_a/S verses reciprocal temperature

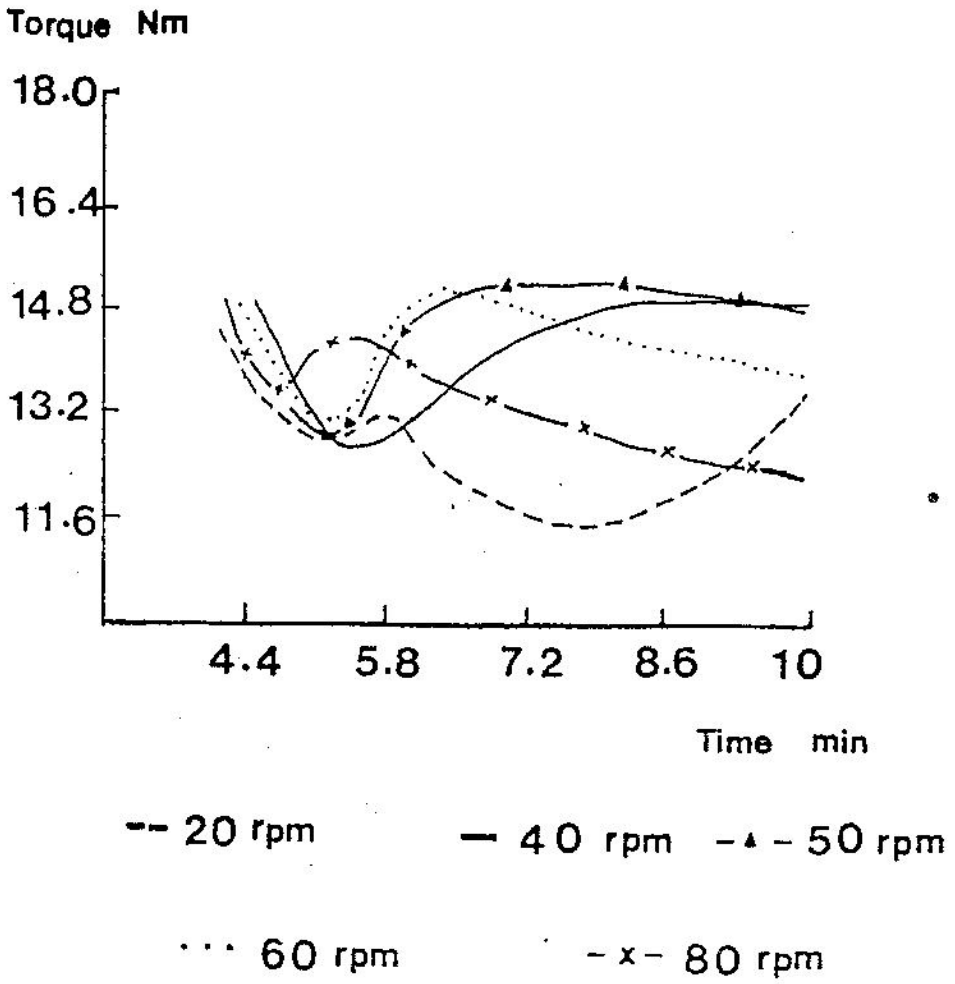

Figure 6: PVC/ENR50/SMR5 (30:10:20) torque profile at various speed against time.